

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-130743

(43)Date of publication of application : 18.05.1999

(51)Int.Cl.

C07C309/10
C07C303/32
C08F 16/14
C25B 13/08
H01M 8/02
// C07B 61/00

(21)Application number : 09-311776

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(22)Date of filing : 13.11.1997

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(30)Priority

Priority number : 09230143 Priority date : 27.08.1997 Priority country : JP

(54) PRODUCTION OF PERFLUOROALKYLVINYL ETHER DERIVATIVE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a method for producing the aimed functional group-bearing perfluoroalkylvinyl ether derivative in high yield at low cost by suppressing cyclization as the main factor of lowering its yield.

SOLUTION: This method for producing the aimed compound comprises the following process: a perfluoroalkylvinyl ether iodide of the formula $\text{CF}_2=\text{CF}(\text{OCF}_2\text{CFY})_n\text{OCF}_2\text{CF}_2\text{I}$ (Y is F or trifluoromethyl; (n) is an integer of 1-3) is subjected to sodium bisulfite in the presence of zinc or a zinc-copper-based alloy in a polar solvent to obtain the objective compound of the formula $\text{CF}_2=\text{CF}(\text{OCF}_2\text{CFY})_n\text{OCF}_2\text{CF}_2\text{SO}_3\text{Na}$.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than

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[Date of final disposal for application]

[Patent number]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to the manufacture method of a perfluoro-alkyl vinyl ether derivative of having a functional group.

[0002]

[Description of the Prior Art] The perfluoro-alkyl vinyl ether derivative which has a functional group is useful as a functional-group monomer for manufacturing ion exchange membrane, and the high molecular compound which has functionality can be manufactured by introducing a sulfonic group. The various usage can be considered based on the ion-exchange nature of this sulfonic group, and it is used for a fuel cell, moisture solution equipment, etc. as a solid-state polyelectrolyte film.

[0003] The acid fluoride which has a functional group is made to react with hexafluoro propene oxide (HFPO) conventionally as the manufacture method of perfluoro-alkyl vinyl ether of having the above-mentioned sulfonic acid type functional group, and the method of manufacturing the perfluoro-alkyl vinyl ether derivative which pyrolyzes the obtained epoxy addition product and has a functional group is learned.

[0004]

[Problem(s) to be Solved by the Invention] However, the manufacture method of a perfluoro-alkyl vinyl ether derivative of having this functional group has the following troubles, and has the problem that cost becomes high.

** A special production process is needed for composition of the acid fluoride which has the functional group which is a raw material, and the purchase of these reagents is difficult for it.

** When the epoxy addition product which has the functional group of a raw material tends to be pyrolyzed and it is going to compound the specified substance, since the compound which changed with ring closure arises, yield is low.

[0005] This invention suppresses generating of the ring closure which is the key factor to which yield is reduced, and aims at offering the method of manufacturing cheaply the perfluoro-alkyl vinyl ether derivative which has the target functional group by high yield.

[0006]

[Means for Solving the Problem] A manufacture method of a perfluoro-alkyl vinyl ether derivative of this invention which solves said technical problem $\text{CF}_2 = \text{CF}(\text{OCF}_2 \text{ CFY})_n \text{OCF}_2 \text{ CF}_2 \text{I}$ (however, Y in a formula expresses a fluorine or a trifluoromethyl radical, and n expresses an integer of 1-3.) It is characterized by obtaining a compound which a sodium hydrogensulfite is made to act on iodation perfluoro-alkyl vinyl ether expressed under existence of a zinc or zinc-copper system alloy and in a polar solvent, and is expressed with $\text{CF}_2 = \text{CF}(\text{OCF}_2 \text{ CFY})_n \text{OCF}_2 \text{ CF}_2 \text{SO}_3 \text{Na}$.

[0007]

[Embodiment of the Invention] Hereafter, the operation gestalt of the manufacture method of the perfluoro-alkyl vinyl ether derivative concerning this invention is explained.

[0008] This invention makes iodation perfluoro-alkyl vinyl ether and a sodium hydrogensulfite react as

an active metal under the existence in the end of a zinc or zinc-copper system alloy powder.

[0009] an acid full ora [like / here / iodation difluoro acetyl full ORAIDO (ICF2 CFO)] whose iodation perfluoro-alkyl vinyl ether used as a raw material is -- the id -- a compound and a hexafluoro pro PENKIKI side -- the caesium full ora in tetraglyme -- it can obtain by pyrolyzing the compound which reacted as a catalyst and was obtained in the id at 250 degrees C after alkali treatment.

[0010] As for the zinc or zinc-copper system alloy to add, it is desirable to present a reaction by powder in order to make [many] an active site. Here, the compounding ratio of a zinc-copper system alloy has the desirable range of 1:1 to 1:0.01 at a mole ratio. This is because the reaction rate of the reaction made into the purpose falls by the fall of the content of this zinc contributed to a reaction as it is out of range, so it is not desirable. Moreover, since copper can fall out to reaction time and activity zinc can be obtained if the above-mentioned zinc-copper system alloy is added, improvement in a reaction rate can be aimed at rather than a zinc independent thing.

[0011] This reaction temperature usually has the desirable range of 20 degrees C - 100 degrees C, although a desirable range is suitably adopted by the class of raw material. It is because advance of a reaction is slow, it is necessary to use a pressure vessel, equipment becomes large-scale and yield is not industrially desirable, if it becomes it low that this is less than 20 degrees C and reaction temperature is made high on the other hand exceeding 100 degrees C.

[0012] As a solvent to be used, alcohol / water mixed solvent is desirable, and can mention lower alcohol (a methanol, ethanol, propanol, etc.) as the above-mentioned alcohol. It is because water is required for considering as alcohol / water mixed solvent here in order to dissolve the sodium hydrogensulfite used for a reaction and to advance a reaction smoothly.

[0013] Especially as an addition of the water to alcohol, 1:0.2 to 1:0.4 is [1:0.05 to about 1:1] desirable at a capacity factor. This is because the solubility of iodation perfluoro-alkyl vinyl ether falls that it is out of range, and a reaction does not fully progress, so the yield of the iodation perfluoro-alkyl vinyl ether derivative made into the purpose falls and it is not [this] desirable.

[0014] The addition of the sodium hydrogensulfite to iodation perfluoro-alkyl vinyl ether is 1-3, especially 1.5-2.5 at a mole ratio. It is desirable. If there are few amounts of the sodium hydrogensulfite to iodation perfluoro-alkyl vinyl ether at a mole ratio than 1, a reaction will not fully progress, but unreacted iodation perfluoro-alkyl vinyl ether will remain, this poses a problem, on the other hand, does not have a reaction top merit only by sodium hydrogensulfites unnecessary in the system of reaction increasing in number, in exceeding 3 by the mole ratio, also industrially, serves as the cost high, and is both because it is not desirable. Moreover, as for especially the addition of the zinc to iodation perfluoro-alkyl vinyl ether, or a zinc-copper system alloy, 1.5-3 is [one or more] desirable at a mole ratio. In order not to fulfill the amount of active metals required for a reaction with the case where a mole ratio is smaller than 1, a reaction does not fully progress, but unreacted iodation perfluoro-alkyl vinyl ether remains, this is a problem, on the other hand, does not have a reaction top merit only by unnecessary active metals increasing in number to the system of reaction by the case where a mole ratio exceeds 3, also industrially, serves as the cost high, and is both because it is not desirable. The perfluoro-alkyl vinyl ether derivative which iodation perfluoro-alkyl vinyl ether reacts with zinc, and is considered to form the zinc iodide compound by reaction time, reacts to it with a sodium hydrogensulfite through this compound, and has the sulfonic-acid sodium group is generated.

[0015] In an acid or an acid chloride form, the polymerization of the perfluoro-alkyl vinyl ether which has the above-mentioned functional group can be carried out in aqueous data medium using a peroxide system initiator. In manufacture of a copolymer, polymerization temperature has 30 to desirable 100 degrees C. A copolymerization reaction is suppressed as temperature is less than 30 degrees C, this cannot obtain the target copolymer, but on the other hand, even if it heats it exceeding 100 degrees C, it is because equipment becomes large-scale and it is not industrially desirable.

[0016] Moreover, the polymerization pressure force has desirable 2-10kg/cm²G. This is because it is difficult to maintain in the height with which it can be satisfied of a copolymerization reaction rate practically in temperature being the pressurization of under 2kg/cm²G and it cannot obtain the target copolymer. On the other hand, even if it pressurizes exceeding 10kg/cm²G, while the functional-group

concentration in a copolymer becomes low and being connected with performance degradation, it is because it is not industrially desirable in respect of equipment and its actuation.

[0017] The polymer of this invention is a copolymer containing a -SO₃ Na radical, and can be used as the copolymer containing a sulfonic group by carrying out acid treatment of this copolymer. By copolymerizing with other fluorine system olefins, the perfluoro-alkyl vinyl ether which has this functional group is usable as ion exchange membrane which has a functional group, and can be applied as the diaphragm of hydrophilicity, a demarcation membrane, and ion exchange membrane.

[0018]

[Example] Hereafter, the example which shows the effect of this invention is explained with the example of a comparison.

200ml to which the [example of reference] stirrer, the condensator, and the dropping funnel were attached a three-neck flask -- 50ml of carbon tetrachlorides, and a caesium full ora -- id 0.75g It put in and the temperature in a container was kept at 0 degree C. Next, stirring, ICF₂ CFO 10g was dropped slowly and it considered as the caesium alkoxide compound. It is HFPO15g, cooling a cold trap at -80 degrees C. It is adding, 2110.8g of FOCCF(CF₃) OCF₂ CF(CF₃) OCF₂ CF It generates and is ethyl alcohol solution 10wt% of a sodium hydroxide to this compound. After considering as carboxylate in addition, a solvent is distilled, and it heats to 250 **, and is 6.5 g about olefin compound CF₂=CFOCF₂ CF(CF₃) OCF₂ CF₂ I by decarboxylation. It obtained (29% of yield).

[0019] [Example 1] 200ml To a three-neck flask, it is ethanol / water (50ml / 15ml) mixed solvent, and an iodation perfluoro-alkyl vinyl ether compound. They are 4.9 g and 2g of sodium hydrogensulfites about CF₂=CFOCF₂ CF(CF₃) OCF₂ CF₂ I. It puts in and is as an active metal in the end of a zinc-copper system alloy powder. (zinc content 95wt%) 2g It added and the reaction was performed for 75 degrees C - 8 hours. When reaction mixture was filtered, the solid was removed and the solvent was ****(ed) from filtrate, the white compound generated and 3.5g (75% of yield) of CF₂=CFOCF₂ CF(CF₃) OCF₂ CF₂ SO₃ Na which is a perfluoro-alkyl vinyl ether derivative was obtained by repeating recrystallization in water / ethanol mixed solvent in this compound. The obtained product checked that it was the structure of a perfluoro-alkyl vinyl ether derivative by the infrared absorption spectrum and NMR spectrum measurement.

[0020] It sets in the [example 2] example 1, and is 6.6 g as an iodation perfluoro-alkyl vinyl ether compound about CF₂=CFOCF₂ CF(CF₃) OCF₂ CF(CF₃) OCF₂ CF₂ I. It was operated like the example 1 except having added. Consequently, 4.4g (70% of yield) of CF₂=CFOCF₂ CF(CF₃) OCF₂ CF(CF₃) OCF₂ CF₂ SO₃ Na which is a perfluoro-alkyl vinyl ether derivative was obtained.

[0021] the [example 3] example 1 -- setting -- as alcohol -- instead of [of ethanol] -- isopropanol 15ml - - adding -- isopropanol/water (50ml / 15ml) It was operated like the example 1 except having considered as the mixed solvent. Consequently, 3.6g (77% of yield) of CF₂=CFOCF₂ CF(CF₃) OCF₂ CF₂ SO₃ Na which is a perfluoro-alkyl vinyl ether derivative was obtained.

[0022] the [example 4] example 1 -- setting -- zinc content 50wt% it is -- it was operated like the example 1 except having added the zinc-copper system alloy. Consequently, 3.2g (68% of yield) of CF₂=CFOCF₂ CF(CF₃) OCF₂CF₂ SO₃ Na which is a perfluoro-alkyl vinyl ether derivative was obtained.

[0023] It sets in the [example 5] example 1, and is 2g about zinc powder as an active metal. It was operated like the example 1 except having added. Consequently, 2.8g (60% of yield) of CF₂=CFOCF₂ CF(CF₃) OCF₂ CF₂ SO₃ Na which is a perfluoro-alkyl vinyl ether derivative was obtained.

[0024] [Example 1 of a comparison] 200ml To a three-neck flask, they are 4.9 g and a sodium hydrogensulfite about CF₂=CFOCF₂ CF(CF₃) OCF₂ CF₂ I as ethanol / water (50ml / 15ml) mixed solvent, and an iodation perfluoro-alkyl vinyl ether compound. 2g The reaction was performed for 75 degrees C - 8 hours without having added and adding a zinc-copper system alloy. After having filtered reaction mixture, removing the solid and ****(ing) a solvent from filtrate, although recrystallization was repeated in water / ethanol mixed solvent, the product was not accepted in this compound.

[0025] In the [example 2 of comparison] example 1, it was operated like the example 1 except having considered as the ethanol independent solvent as a solvent. Consequently, only 1.0g (21% of yield) of CF₂=CFOCF₂ CF(CF₃) OCF₂ CF₂ SO₃ Na which is a perfluoro-alkyl vinyl ether derivative was not

obtained.

[0026] [Application 1] content volume 300 cm³ 80ml of deoxidation water was put in into the autoclave made from stainless steel, CF₂=CFOCF₂ CF(CF₃) OCF₂ CF₂ SO₃ Na 3g, 0.15g [of ammonium peroxydisulfates], and isopropyl alcohol 5ml was added into this, tetrafluoroethylene gas replaced the inside of a container, 5kg/cm²G was held, and it was made to react at 60 degrees C under stirring for 8 hours. Unreacted tetrafluoroethylene gas is emitted after reaction termination, the products currently distributed underwater are collected, and it is copolymer 3.4 g. It obtained. The obtained copolymer checked that it was functional-group concentration % of the copolymer of 14 mols by the infrared absorption spectrum and NMR spectrum measurement.

[0027] [Application 2] content volume 300 cm³ 80ml of deoxidation water is put in into the autoclave made from stainless steel, and they are CF₂=CFOCF₂ CF(CF₃) OCF₂ CF(CF₃) OCF₂ CF₂ SO₃ Na 3g and 0.1g of ammonium peroxydisulfates in this. And isopropyl alcohol 5ml is added and tetrafluoroethylene gas replaces the inside of a container. 5kg/cm²G was held and it was made to react at 60 degrees C under stirring for 8 hours. After reaction termination, unreacted tetrafluoroethylene gas is emitted, products are collected, and it is copolymer 2.6 g. It obtained. The obtained copolymer checked that it was functional-group concentration % of the copolymer of 17 mols by the infrared absorption spectrum and NMR spectrum measurement.

[0028]

[Effect of the Invention] In this invention, CF₂=CF(OCF₂ CFY) _n OCF₂ CF₂ I (However, Y in a formula expresses a fluorine or a trifluoromethyl radical, and n expresses the integer of 1-3.) The compound which a sodium hydrogensulfite is made to act on the iodation perfluoro-alkyl vinyl ether expressed under existence of a zinc or zinc-copper system alloy and in a polar solvent, and is expressed with CF₂=CF(OCF₂CFY) _n OCF₂ CF₂ SO₃ Na was obtained. Therefore, decline in the yield by the ring closure at the time of heat differentiation is suppressed, and it becomes possible to obtain cheaply the perfluoro-alkyl vinyl ether compound which has the target functional group by high yield.

[0029] Moreover, it becomes possible to apply as the diaphragm of a hydrophilic group, a demarcation membrane, and ion exchange membrane by copolymerizing the obtained perfluoro-alkyl vinyl ether derivative with a fluorine system olefin.

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EFFECT OF THE INVENTION

[Effect of the Invention] In this invention, $\text{CF}_2=\text{CF}(\text{OCF}_2\text{CFY})_n\text{OCF}_2\text{CF}_2\text{I}$ however, Y in a formula expresses a fluorine or a trifluoromethyl radical, and n expresses the integer of 1-3 -- The compound which a sodium hydrogensulfite is made to act on the iodation perfluoro-alkyl vinyl ether expressed under existence of a zinc or zinc-copper system alloy and in a polar solvent, and is expressed with $\text{CF}_2=\text{CF}(\text{OCF}_2\text{CFY})_n\text{OCF}_2\text{CF}_2\text{SO}_3\text{Na}$ was obtained. Therefore, decline in the yield by the ring closure at the time of heat differentiation is suppressed, and it becomes possible to obtain cheaply the perfluoro-alkyl vinyl ether compound which has the target functional group by high yield.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] However, the manufacture method of a perfluoro-alkyl vinyl ether derivative of having this functional group has the following troubles, and has the problem that cost becomes high.

** A special production process is needed for composition of the acid fluoride which has the functional group which is a raw material, and the purchase of these reagents is difficult for it.

** When the epoxy addition product which has the functional group of a raw material tends to be pyrolyzed and it is going to compound the specified substance, since the compound which changed with ring closure arises, yield is low.

[0005] This invention suppresses generating of the ring closure which is the key factor to which yield is reduced, and aims at offering the method of manufacturing cheaply the perfluoro-alkyl vinyl ether derivative which has the target functional group by high yield.

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MEANS

[Means for Solving the Problem] A manufacture method of a perfluoro-alkyl vinyl ether derivative of this invention which solves said technical problem $\text{CF}_2=\text{CF}(\text{OCF}_2\text{CFY})_n\text{OCF}_2\text{CF}_2\text{I}$ (however, Y in a formula expresses a fluorine or a trifluoromethyl radical, and n expresses an integer of 1-3 --) It is characterized by obtaining a compound which a sodium hydrogensulfite is made to act on iodation perfluoro-alkyl vinyl ether expressed under existence of a zinc or zinc-copper system alloy and in a polar solvent, and is expressed with $\text{CF}_2=\text{CF}(\text{OCF}_2\text{CFY})_n\text{OCF}_2\text{CF}_2\text{SO}_3\text{Na}$.

[0007]

[Embodiment of the Invention] Hereafter, the operation gestalt of the manufacture method of the perfluoro-alkyl vinyl ether derivative concerning this invention is explained.

[0008] This invention makes iodation perfluoro-alkyl vinyl ether and a sodium hydrogensulfite react as an active metal under the existence in the end of a zinc or zinc-copper system alloy powder.

[0009] an acid full ora [like / here / iodation difluoro acetyl full ORAIDO (ICF_2CFO)] whose iodation perfluoro-alkyl vinyl ether used as a raw material is -- the id -- a compound and a hexafluoro pro PENKIKI side -- the caesium full ora in tetraglyme -- it can obtain by pyrolyzing the compound which reacted as a catalyst and was obtained in the id at 250 degrees C after alkali treatment.

[0010] As for the zinc or zinc-copper system alloy to add, it is desirable to present a reaction by powder in order to make [many] an active site. Here, the compounding ratio of a zinc-copper system alloy has the desirable range of 1:1 to 1:0.01 at a mole ratio. This is because the reaction rate of the reaction made into the purpose falls by the fall of the content of this zinc contributed to a reaction as it is out of range, so it is not desirable. Moreover, since copper can fall out to reaction time and activity zinc can be obtained if the above-mentioned zinc-copper system alloy is added, improvement in a reaction rate can be aimed at rather than a zinc independent thing.

[0011] This reaction temperature usually has the desirable range of 20 degrees C - 100 degrees C, although a desirable range is suitably adopted by the class of raw material. It is because advance of a reaction is slow, it is necessary to use a pressure vessel, equipment becomes large-scale and yield is not industrially desirable, if it becomes it low that this is less than 20 degrees C and reaction temperature is made high on the other hand exceeding 100 degrees C.

[0012] As a solvent to be used, alcohol / water mixed solvent is desirable, and can mention lower alcohol (a methanol, ethanol, propanol, etc.) as the above-mentioned alcohol. It is because water is required for considering as alcohol / water mixed solvent here in order to dissolve the sodium hydrogensulfite used for a reaction and to advance a reaction smoothly.

[0013] Especially as an addition of the water to alcohol, 1:0.2 to 1:0.4 is [1:0.05 to about 1:1] desirable at a capacity factor. This is because the solubility of iodation perfluoro-alkyl vinyl ether falls that it is out of range, and a reaction does not fully progress, so the yield of the iodation perfluoro-alkyl vinyl ether derivative made into the purpose falls and it is not [this] desirable.

[0014] The addition of the sodium hydrogensulfite to iodation perfluoro-alkyl vinyl ether is 1-3, especially 1.5-2.5 at a mole ratio. It is desirable. If there are few amounts of the sodium hydrogensulfite to iodation perfluoro-alkyl vinyl ether at a mole ratio than 1, a reaction will not fully progress, but

unreacted iodation perfluoro-alkyl vinyl ether will remain, this poses a problem, on the other hand, does not have a reaction top merit only by sodium hydrogensulfites unnecessary in the system of reaction increasing in number, in exceeding 3 by the mole ratio, also industrially, serves as the cost high, and is both because it is not desirable. Moreover, as for especially the addition of the zinc to iodation perfluoro-alkyl vinyl ether, or a zinc-copper system alloy, 1.5-3 is [one or more] desirable at a mole ratio. In order not to fulfill the amount of active metals required for a reaction with the case where a mole ratio is smaller than 1, a reaction does not fully progress, but unreacted iodation perfluoro-alkyl vinyl ether remains, this is a problem, on the other hand, does not have a reaction top merit only by unnecessary active metals increasing in number to the system of reaction by the case where a mole ratio exceeds 3, also industrially, serves as the cost high, and is both because it is not desirable. The perfluoro-alkyl vinyl ether derivative which iodation perfluoro-alkyl vinyl ether reacts with zinc, and is considered to form the zinc iodide compound by reaction time, reacts to it with a sodium hydrogensulfite through this compound, and has the sulfonic-acid sodium group is generated.

[0015] In an acid or an acid chloride form, the polymerization of the perfluoro-alkyl vinyl ether which has the above-mentioned functional group can be carried out in aqueous medium using a peroxide system initiator. In manufacture of a copolymer, polymerization temperature has 30 to desirable 100 degrees C. A copolymerization reaction is suppressed as temperature is less than 30 degrees C, this cannot obtain the target copolymer, but on the other hand, even if it heats it exceeding 100 degrees C, it is because equipment becomes large-scale and it is not industrially desirable.

[0016] Moreover, the polymerization pressure force has desirable 2-10kg/cm²G. This is because it is difficult to maintain in the height with which it can be satisfied of a copolymerization reaction rate practically in temperature being the pressurization of under 2kg/cm²G and it cannot obtain the target copolymer. On the other hand, even if it pressurizes exceeding 10kg/cm²G, while the functional-group concentration in a copolymer becomes low and being connected with performance degradation, it is because it is not industrially desirable in respect of equipment and its actuation.

[0017] The polymer of this invention is a copolymer containing a -SO₃ Na radical, and can be used as the copolymer containing a sulfonic group by carrying out acid treatment of this copolymer. By copolymerizing with other fluorine system olefins, the perfluoro-alkyl vinyl ether which has this functional group is usable as ion exchange membrane which has a functional group, and can be applied as the diaphragm of hydrophilicity, a demarcation membrane, and ion exchange membrane.

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EXAMPLE

[Example] Hereafter, the example which shows the effect of this invention is explained with the example of a comparison.

200ml to which the [example of reference] stirrer, the condensator, and the dropping funnel were attached a three-neck flask -- 50ml of carbon tetrachlorides, and a caesium full ora -- id 0.75g It put in and the temperature in a container was kept at 0 degree C. Next, stirring, ICF2 CFO 10g was dropped slowly and it considered as the caesium alkoxide compound. It is HFPO15g, cooling a cold trap at -80 degrees C. It is adding, 2I10.8g of FOCCF(CF3) OCF2 CF(CF3) OCF2 CF It generates and is ethyl alcohol solution 10wt% of a sodium hydroxide to this compound. After considering as carboxylate in addition, a solvent is distilled, and it heats to 250 **, and is 6.5 g about olefin compound CF2 =CFOCF2 CF(CF3) OCF2 CF2 I by decarboxylation. It obtained (29% of yield).

[0019] [Example 1] 200ml To a three-neck flask, it is ethanol / water (50ml / 15ml) mixed solvent, and an iodation perfluoro-alkyl vinyl ether compound. They are 4.9 g and 2g of sodium hydrogensulfites about CF2 =CFOCF2 CF(CF3) OCF2 CF2 I. It puts in and is as an active metal in the end of a zinc-copper system alloy powder. (zinc content 95wt%) 2g It added and the reaction was performed for 75 degrees C - 8 hours. When reaction mixture was filtered, the solid was removed and the solvent was ****(ed) from filtrate, the white compound generated and 3.5g (75% of yield) of CF2 =CFOCF2 CF(CF3) OCF2 CF2 SO3 Na which is a perfluoro-alkyl vinyl ether derivative was obtained by repeating recrystallization in water / ethanol mixed solvent in this compound. The obtained product checked that it was the structure of a perfluoro-alkyl vinyl ether derivative by the infrared absorption spectrum and NMR spectrum measurement.

[0020] It sets in the [example 2] example 1, and is 6.6 g as an iodation perfluoro-alkyl vinyl ether compound about CF2 =CFOCF2 CF(CF3) OCF2 CF(CF3) OCF2 CF2 I. It was operated like the example 1 except having added. Consequently, 4.4g (70% of yield) of CF2 =CFOCF2 CF(CF3) OCF2 CF(CF3) OCF2 CF2 SO3 Na which is a perfluoro-alkyl vinyl ether derivative was obtained.

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[0022] the [example 4] example 1 -- setting -- zinc content 50wt% it is -- it was operated like the example 1 except having added the zinc-copper system alloy. Consequently, 3.2g (68% of yield) of CF2 =CFOCF2 CF(CF3) OCF2 CF2 SO3 Na which is a perfluoro-alkyl vinyl ether derivative was obtained.

[0023] It sets in the [example 5] example 1, and is 2g about zinc powder as an active metal. It was operated like the example 1 except having added. Consequently, 2.8g (60% of yield) of CF2 =CFOCF2 CF(CF3) OCF2 CF2 SO3 Na which is a perfluoro-alkyl vinyl ether derivative was obtained.

[0024] [Example 1 of a comparison] 200ml To a three-neck flask, they are 4.9 g and a sodium hydrogensulfite about CF2 =CFOCF2 CF(CF3) OCF2 CF2 I as ethanol / water (50ml / 15ml) mixed solvent, and an iodation perfluoro-alkyl vinyl ether compound. 2g The reaction was performed for 75 degrees C - 8 hours without having added and adding a zinc-copper system alloy. After having filtered

reaction mixture, removing the solid and ****(ing) a solvent from filtrate, although recrystallization was repeated in water / ethanol mixed solvent, the product was not accepted in this compound.




















[0025] In the [example 2 of comparison] example 1, it was operated like the example 1 except having considered as the ethanol independent solvent as a solvent. Consequently, only 1.0g (21% of yield) of $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_3\text{Na}$ which is a perfluoro-alkyl vinyl ether derivative was not obtained.

[0026] [Application 1] content volume 300 cm³ 80ml of deoxidation water was put in into the autoclave made from stainless steel, $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_3\text{Na}$ 3g, 0.15g [of ammonium peroxydisulfates], and isopropyl alcohol 5ml was added into this, tetrafluoroethylene gas replaced the inside of a container, 5kg/cm²G was held, and it was made to react at 60 degrees C under stirring for 8 hours. Unreacted tetrafluoroethylene gas is emitted after reaction termination, the products currently distributed underwater are collected, and it is copolymer 3.4 g. It obtained. The obtained copolymer checked that it was functional-group concentration % of the copolymer of 14 mols by the infrared absorption spectrum and NMR spectrum measurement.










[0027] [Application 2] content volume 300 cm³ 80ml of deoxidation water is put in into the autoclave made from stainless steel, and they are $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_3\text{Na}$ 3g and 0.1g of ammonium peroxydisulfates in this. And isopropyl alcohol 5ml is added and tetrafluoroethylene gas replaces the inside of a container. 5kg/cm²G was held and it was made to react at 60 degrees C under stirring for 8 hours. After reaction termination, unreacted tetrafluoroethylene gas is emitted, products are collected, and it is copolymer 2.6 g. It obtained. The obtained copolymer checked that it was functional-group concentration % of the copolymer of 17 mols by the infrared absorption spectrum and NMR spectrum measurement.

[Translation done.]

ZALUKAEVA, TATYANA Docket: Regular Amended (28 items sorted by NONE in NO order)

Phx	App #	Fwd-to-Exmr	Status	Loc	Chrg To Loc	Class	Subclass	Mo-Old	Unavail	Type
	10/419285	01/22/2004	71	e	e	526	086.000	1	-	-
	10/400331	01/14/2004	71	e	e	526	319.000	1+	-	-
	10/395937	01/21/2004	71	e	e	526	317.100	1	-	-
	10/377440	01/29/2004	71	e	e	526	319.000	1	-	-
	10/317575	01/13/2004	71	e	e	526	317.100	1+	-	-
	10/299299	02/10/2004	71	e	e	521	025.000	-1	-	-
	10/293022	02/03/2004	71	e	e	526	219.600	1	-	-
	10/275495	01/30/2004	71	e	e	526	217.000	1	-	-
	10/262985	01/15/2004	71	e	e	526	317.100	1+	-	-
	10/200192	01/21/2004	71	e	e	526	319.000	1	-	-
	10/197684	02/13/2004	71	e	e	526	218.100	-1	-	-
	10/182593	01/14/2004	71	e	e	526	319.000	1+	-	-
	10/178474	01/14/2004	71	e	e	526	258.000	1+	-	-
	10/142502	02/13/2004	71	e	e	526	319.000	-1	-	-
	10/136534	01/16/2004	71	e	e	526	070.000	1+	-	-
	10/135798	02/04/2004	71	e	e	521	033.000	-1	-	-
	10/129942	02/02/2004	71	e	e	526	319.000	1	-	-
	10/121518	02/20/2004	71	e	e	526	320.000	-1	-	-
	10/108916	01/21/2004	71	e	e	528	402.000	1	-	-

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Phx	App #	Fwd-to-Exmr	Status	Loc	Chrg To Loc	Class	Subclass	Mo-Old	Unavail	Type
	10/089240	02/02/2004	71	e	e	526	319.000	1	-	-
	10/088107	01/07/2004	71	e	e	526	240.000	1+	-	-
	10/059650	02/11/2004	71	e	e	521	033.000	-1	-	-
	10/045725	01/15/2004	71	e	e	526	317.100	1+	-	-
	10/000913	01/20/2004	71	e	e	526	320.000	1+	-	-
	09/959800	12/30/2003	71	e	e	526	064.000	2	-	-
	09/917674	02/11/2004	71	e	e	526	320.000	-1	-	-
	09/889571	02/12/2004	71	e	e	526	308.000	-1	-	-
	09/508378	02/13/2004	71	e	e	526	341.000	-1	-	-